

**Scientific Report**  
Dec. 2015– Dec. 2016

**New metal complexes with metal-chalcogen bonds - potential precursors for electronic materials. code PN-II-ID-PCE\_2011-3-0659**

The objectives accomplished during this period were as followings, according to the proposed research project:

- Synthesis and structural characterization of several new organometallic (Sb, Bi or Sn) compounds with organochalcogen- or alkoxo ligands.
- New complexes of *d* metals with organo-chalcogen (Se, Te) ligands. Synthesis and structural characterization.
- Thermal behavior of the new precursors and preliminary studies regarding their vapor deposition. Structural and morphological characterization of the thin films.
- Structural characterization of the obtained nanopowders
- Final characterization of several compounds obtained before 2016.
- Dissemination of the results, manuscripts' preparation.

The new compounds were characterized by multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{77}\text{Se}$ ,  $^{125}\text{Te}$ , as appropriate) and mass spectrometry. Part of them were characterized by IR spectroscopy, powder or single-crystal X-ray diffraction. 2D NMR experiments (COSY, HSQC, HMBC) were used to assign the resonances for several of the investigated species and the dynamic behavior in solution of some compounds was studied by variable temperature NMR. Majority of the reactions were performed under argon atmosphere, using dry and freshly distilled solvents, in order to avoid the decomposition either of the starting materials or the products by aerial oxidation or hydrolysis.

**1. Synthesis and structural characterization of new organometallic (Bi or Sn) compounds with organochalcogen (Se, Te) ligands.**

New organo Bi(III) compounds of type  $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{E}]\text{BiX}$  ( $\text{E} = \text{S}, \text{Se}$ ,  $\text{X} = \text{SCN}^-, \text{SeCN}^-, \text{S}_2\text{CNMe}_2^-$  or  $\text{Se}_2\text{CNMe}_2^-$ ) were prepared by salt metathesis reactions. Several diorganotin(IV) compounds with dithio- or diselenocarbamate ligands were also obtained by reacting

diorganotin(IV) halides or pseudo-halides with the appropriate sodium salt in 1 : 1 or 1 : 2 molar ratio.. Several analytical data for the investigated compounds are given in Table 1.

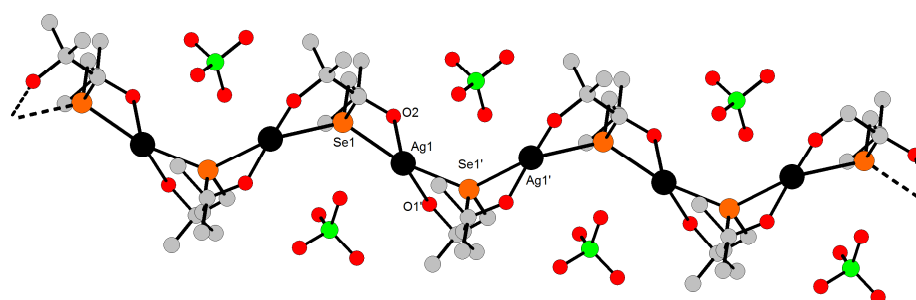
**Table 1.** Analytical data for the investigated tin(IV) compounds

No.	Compus	$\eta$ [%]	m.p. [°C]	$^{119}\text{Sn}$ NMR, $\delta$ [ppm]
1	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{PhSnCl}_2$	58.4	135	-170.0
2	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]^n\text{BuSnCl}_2$	60.0	150	103.0
3	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$	70.0	227	-257.7
4	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{PhSnCl}(\text{NCS})$	75.3	-	-242.6
5	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}(\text{NCS})$	58.4	248	-330.0
6	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}(\text{NCSe})$	65.3	-	-329.5
7	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{PhSn}(\text{NCS})_2$	70.5	-	-329.3
8	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]^n\text{BuSn}(\text{NCS})_2$	64.0	110	-266.6
9	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})_2$	90.5	248	-398.4
10	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCSe})_2$	81.0	187	-406.4
11	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})(\text{S}_2\text{CNMe}_2)$	68.0	196	-366.9
12	$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})(\text{S}_2\text{CNEt}_2)$	82.0	-	-359.5

## 2. New group 11 (Cu, Ag) metal complexes with dialkoxo ligands

Ligands of type  $[\text{R}_2\text{C}(\text{OH})\text{CH}_2]_2\text{E}$  ( $\text{R} = \text{Me}, \text{Ph}$ ;  $\text{E} = \text{Se}, \text{Te}$ ) were used both in protonated and deprotonated form in order to obtain Cu(I) or Ag(I) metal complexes.

The multinuclear NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{77}\text{Se}$  and  $^{125}\text{Te}$ , as appropriate) clearly evidenced the formation of the metal complexes  $[\text{Me}_2\text{C}(\text{OH})\text{CH}_2]_2\text{E}(\text{AgX})_2$  ( $\text{E} = \text{Se}, \text{Te}$ ;  $\text{X} = \text{OTf}, \text{ClO}_4$ ). Single-crystal X-ray diffraction studies revealed a polymeric structure for  $[\text{Me}_2\text{C}(\text{OH})\text{CH}_2]_2\text{Se}(\text{AgClO}_4)_2$ , as depicted in Figure 1.



**Figure 1.** Polymeric association in  $[\text{Me}_2\text{C}(\text{OH})\text{CH}_2]_2\text{Se}(\text{AgClO}_4)_2$

## 3. New group 12 (Zn, Cd) metal complexes with organo-chalcogen ligands

(a) Zinc and cadmium pseudo-halides stabilized by triorganophosphanes of type  $[(2-\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_{3-x}\text{P}$  ( $x = 1, 2$ )  $[(2-\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_{3-x}\text{P}$  ( $x = 1, 2$ ) were prepared by exchanging chlorine in  $[(2-\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_{3-x}\text{PMCl}_2$  with  $\text{SCN}^-$  or  $\text{SeCN}^-$  ligands.

(b) Both homoleptic and heteroleptic group 12 metal complexes with ligands of type  $[R_2C(OH)CH_2]E[C_6H_4CH_2NMe_2]$  ( $R = Me, CF_3$ ,  $E = S, Se$ ) were prepared by amide elimination reactions. The molecular structures of the ligand  $[(CF_3)_2C(OH)CH_2]Se[C_6H_4CH_2NMe_2]$  and for several Zn and Cd complexes were determined by single-crystal X-ray diffraction.

#### 4. Zinc- and copper-zinc ferrite preparation using oxalate precursors

Zinc- and copper substituted zinc ferrites were obtained from oxalate precursors and several methods were used in order to establish the best strategy for the synthesis of  $ZnFe_2O_4$  and  $Cu_{0.5}Zn_{0.5}Fe_2O_4$ .

The metal precursors,  $MC_2O_4 \cdot xH_2O$  ( $M = Cu, Zn, Fe$ ) were precipitated from aqueous solutions, using the appropriate metal salts and  $(NH_4)_2C_2O_4 \cdot H_2O$  as reagents. The single-source precursors were coprecipitated from solution or solid state, using the same reagents. Further, the individual precursors were physically mixed in water suspension or mechanochemically mixed in a mortar. The thermal behaviour of all precursors was investigated and it was observed that all precursors decompose into metal oxides below  $500^\circ C$ . It was also proved that coprecipitation of precursors slightly narrows the decomposition thermal range, from approx.  $100\text{--}450^\circ C$  to  $150\text{--}400^\circ C$ . FT-IR spectroscopy was used to monitor the chemical reactions. Further investigations by powder XRD will complete the present work by establishing the exact nature of the resulting oxides.

#### Publications

1. Bis(2-phenoxyphenyl)dichalcogenides and their chemical reactivity.,  
A. M. Toma, A. Nicoara, A. Silvestru, T. Rüffer, H. Lang and M. Mehring,  
*J. Organomet. Chem.*, **2016**, 810, 33-39. doi.org/10.1016/j.jorganchem.2016.03.002.
2. Heterocyclic bismuth(III) compounds with transannular S→Bi interactions. An experimental and theoretical approach.  
A. M. Toma, C. I. Rat, A. Silvestru, T. Rüffer, H. Lang and M. Mehring,  
*J. Organomet. Chem.*, **2016**, 806, 5-11, doi.org/10.1016/j.jorganchem.2016.01.019.
3. Cobalt(II) complexes of organophosphorus ligands with XPNSO skeleton ( $X = O, S$ ). Solid state structure and solution behavior.  
E. Denes, A. Pöllnitz, F. Cziple, M. Vlassa and A. Silvestru,  
*Inorg. Chim. Acta*, **2016**, 444, 23-28, doi:10.1016/j.ica.2016.01.018.
4. Silver(I) complexes of a new multidentate macrocyclic ligand with N/S/Se donor atoms.  
R. A. Popa, A. Silvestru and A. Pop,  
*Polyhedron*, **2016**, 110, 197-202, doi:10.1016/j.poly.2016.02.045.
5. New hypervalent organoselenium compounds with O→Se intramolecular interactions.  
R. A. Popa, A. Pop, C. Silvestru and A. Silvestru, *Rev. Roum. Chim.*, **2016**, 61(6-7), 495-501.
6. New diorganochalcogen compounds based on the 2-( $Me_2NCH_2$ ) $C_6H_4$  group.  
B. Danciu, R. A. Popa, A. Pop, V. Zaharia, C. Silvestru and A. Silvestru,  
*Studia Universitatis Babes-Bolyai, Seria Chimia*, **2016**, LXI, 3 (1), 19-28.

7. Organoselenium compounds with (N,C,N) pincer ligands. Structure and chemical behaviour.  
A. Pop, A. Silvestru, *J. Organomet. Chem.*, in preparation.
8. Cadmium complexes bearing  $\text{Me}_2\text{N}^+\text{E}^-\text{O}^-$  (E = S, Se) organochalcogenolates and their zinc and mercury analogues  
A. Pop, C. Bellini, V. Dorcet, T. Roisnel, J.-F. Carpentier, A. Silvestru, Y. Sarazin, *Dalton Trans.*, in preparation.
9. Group 12 metal complexes with triarylphosphanes of type  $\text{PR}_x\text{Ph}_{3-x}$   
[R = 2-( $\text{Me}_2\text{NCH}_2$ ) $\text{C}_6\text{H}_4$ , 2-{ $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2$ } $\text{C}_6\text{H}_4$ , x = 1 - 3],  
A. Covaci, R. Suteu, I. Covaci, A. Silvestru, *Dalton Trans.*, in preparation.
10. Diorganochalcogen (S, Se, Te) ligands with alkoxo functionalities and their group 11 (Cu, Ag) metal complexes,  
R. Mitea, A. Silvestru, *Polyhedron*, in preparation.
11. Synthetic strategies for zinc- and copper-zinc ferrite preparation using oxalate precursors.  
M. Venter, I. E. Nagy, A. L. Erdei-Ardeleanu, F. Goga, M. Nasui, *J. Thermal Analysis and Calorimetry*, in preparation.
12. Diorganotin(IV) compounds with tin–chalcogen bonds. Synthesis and structural characterization.  
C. Coza, N. Chiorean, A. Stegarescu, A. Silvestru, *J. Organomet. Chem.*, in preparation.

## Conferences

1. Synthetic strategies for zinc- and copper-zinc ferrite preparation using oxalate precursors  
M. Venter, I. E. Nagy, A. L. Erdei-Ardeleanu, F. Goga, M. Nasui,  
*a XXXIV-a Conferință Națională de Chimie, cu participare internațională*, 04-07 oct. 2016, Călimănești-Căciulata, Romania, poster presentation.
2. Solution behaviour of hypervalent organotellurium compounds.  
Denes Eleonora, Anca Beleagă, Anca Silvestru,  
Central and Eastern European Bruker Users' Meeting, CEUM, 18 - 20.09.2016, Sofia, Bulgaria, poster presentation.
3. Group 12 Metal Complexes with Organoselenium Ligands  
Alexandra Pop, Anca Silvestru, Clement Bellini, Yann Sarazin,  
*International Conference on the Chemistry of Selenium and Tellurium*, ICCST 13, 23 – 27 Mai, 2016, Gifu, Japonia, poster presentation.
4. Hypervalent Organoselenium Compounds with Alkoxo Functionalities and their Coordination Behavior  
Raluca Mitea, Alexandra Pop, Anca Silvestru,  
*International Conference on the Chemistry of Selenium and Tellurium*, ICCST 13, 23 – 27 Mai, 2016, Gifu, Japonia, oral presentation.
5. New multidentate macrocyclic ligands containing N/O or N/S donor atoms and their metal complexes.  
Alexandra Pop, Anca Silvestru, Vito Lippolis,  
5<sup>th</sup> Workshop of SeS Redox and Catalysis (WSeS-5), 21 – 22 Mai, 2016, Hyratsuka, Japonia, poster presentation.

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Director de proiect  
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